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$L_{2,3}$ XANES OF THE HIGH T_c SUPERCONDUCTOR $YBa_2Cu_3O_{\sim 7}$ WITH VARIABLE OXYGEN CONTENT

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The copper $L_{2,3}$ soft x-ray absorption spectra of the single phase high temperature (T_c=91 K) superconductor $YBa_2Cu_3O_{\sim 7}$ have been measured by using synchrotron radiation at LURE. The spectra show at the absorption threshold a white line at 931.1 eV due to Cu $\underline{2p}3d^{10}$ final states (the underline indicates the hole) for the Cu $3d^9$ initial state, and a broad high energy shoulder with the maximum at 933 eV assigned to Cu $\underline{2p}3d^{10}\underline{L}$ and to Cu $\underline{2p}3d^{10}\underline{L}$ $4s^1$ final states ($\underline{L}$ indicates a hole in the oxygen 2p derived valence band), i.e. to the initial states $3d^9\underline{L}$ and $3d^{10}\underline{L}$. The intensity of this last feature has been found to decrease with decreasing oxygen content x in $YBa_2Cu_3O_{6.5+x}$.

No evidence of Cu $\underline{2p}3d^9$ final states has been found. This experiment gives direct evidence that additional oxygen x does not give Cu^{3+} ions with Cu $3d^8$ configuration but gives $3d^9\underline{L}$ electronic configuration (i.e. $Cu^{2+}O^-$ pairs) and no gap is observed between the $3d^9$ (Cu^+) and $3d^{10}\underline{L}$ configuration (i.e. Cu^+O^- pairs). Therefore in the metallic phase which exhibits superconductivity a continous set of itinerant states $3d^9\underline{L}$ and $3d^{10}\underline{L}$ is observed.

THE ELECTRONIC CONFIGURATION of the copper ions in the high T_c single phase bulk superconductor $YBa_2Cu_3O_{\sim 7}$ is a fundamental point to determine the mechanism of superconductivity in this new material.

Recently, following the discovery of high-T_c superconductivity[1,2] in oxygen deficient perovskites with expected formally mixed valence[3-5], we are living a gold rush toward superconductors with higher and higher critical temperature T_c[6-13]. The presence of the mixed valence of the Cu ions seems to be a strict requirement for the presence of high T_c superconductivity. The mixed valence is obtained by an appropriate ratio of bivalent (Ba) and trivalent (La, Y, Yb,..) ions and the oxygen content. However there is no experimental evidence of Cu^{2+} and Cu^{3+} ions on these materials.

We have focused our attention on the new single phase superconductor $YBa_2Cu_3O_{6.5+x}$ (x~0.4) which exhibits superconductivity above liquid nitrogen temperature. Its structure exhibits two dimensional layers of square planes sharing corners.[13-15] This system is a good conductor for x>0 and show superconductivity below ~90 K. For x>0 the formal valence of Cu is expected to be larger than 2 and mixed valence is expected. For $YBa_2Cu_3O_{\sim 7}$ the formal non integer valence of Cu is v~2.33.

We have used soft x ray absorption spectroscopy as a bulk sensitive method to probe the Cu electronic configurations. High resolution spectra of the absorption threshold of the Cu $L_{2,3}$ soft x-ray absorption have been measured. L_3 (and L_2) soft x-ray absorption is determined by the electronic transitions from the Cu $2p_{3/2}$ (and $2p_{1/2}$) core level to the unoccupied Cu 3d and Cu 4s states selected by dipole selection rule $\Delta l=\pm 1$.

At threshold localized atomic-like final states configurations $\underline{2p}3d^{n+1}$ are expected for a Cu ion with $3d^n$

configuration in the ground state with n<10.[16-18] For Cu^+ compounds with $3d^{10}$ configuration the main final state at threshold is $\underline{2p}3d^{10}4s^1$.[19]

Because of the strong electron hole interaction between the 2p core hole and the 3d electron the energy separation between the $\underline{2p}3d^n$ and $\underline{2p}3d^{n+1}$ final states is of the order of several eV. These final states are a unique probe of the electronic configuration of the Cu ions. In fact $L_{2,3}$ x-ray absorption spectroscopy has been widely used to measure the mixed valence state in the ground state in many compounds.[20,21] Therefore this experimental approach is is a good probe to put to a test the presence of ions with formal oxidation state Cu^{3+} in these systems.

EXPERIMENTAL

The high-T_c superconducting samples have been prepared in Rome University starting from powders of ultra pure Y_2O_3, $BaCO_3$ and CuO. The powder mixture was first fired in air up to 980 °C for 12 hours, then it has been pulverized and pressed into pellets and heated in oxygen at 980 °C for 24 hour. In the last heat treatment the sample has been kept at 5OO °C in oxygen atmosphere for 5 hours. The samples prepared by this procedure show a sharp superconducting transition at about 91K. The structure has been determined by Cu K-edge EXAFS and XANES[15] and the samples have been found to single phase by scanning Auger microscopy:[22]

The experiment has been carried out using as x-ray source the ACO storage ring LURE synchrotron radiation facility in Orsay. A double crystal Beryl 1010 monochromator has been used. The x-ray absorption has been measured by detecting the emitted electron by a channeltron in the total yield mode on both freshly scraped bulk polycrystalline solid and powder samples. In order to observe the effect of the sample reduction by decreasing the oxygen content one powder sample was heated in vacuum for two hours at 400 °C.

RESULTS AND DISCUSSION

Fig.1 shows the Cu $L_{2,3}$ absorption spectra of a bulk $YBa_2Cu_3O_{6.5+x}$ (x~0.4) sample. The white line maximum at the L_3 edge is at 931.1 eV and a shoulder appears at about 933 eV. A similar feature appears about 1.8 eV above the white line maximum at the the L_2 edge.

The white lines at the L_3 and L_2 edges of Cu^{2+} ions are due to atomic like transitions from the ground state Cu $2p^63d^9$ to the final state Cu $2p^53d^{10}$.

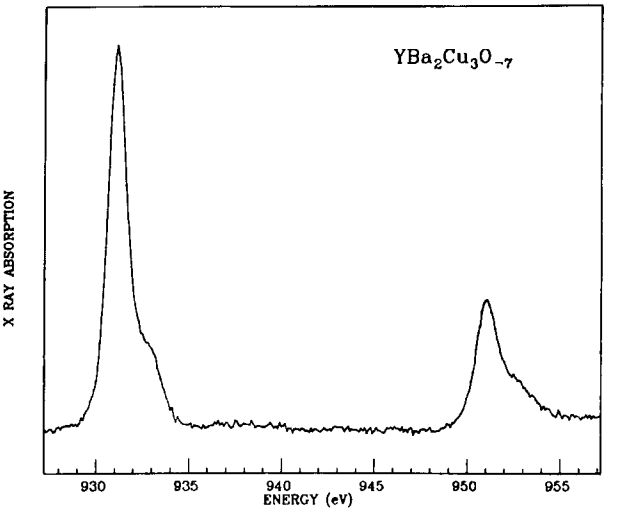

Fig.1 Cu L_3-edge ($2p_{3/2}$) and its spin orbit partner L_2-edge ($2p_{1/2}$) x-ray absorption spectrum measured by electron total yield of bulk high T_c superconductor $YBa_2Cu_3O_{6.9}$ sample with T_c=91K.

In order to assign the final state configurations of the two shoulders at 1.8 eV above the white line we have compared the L_3 spectrum of $YBa_2Cu_3O_{6.5+x}$ (x~0.4) with model compounds with expected integer valence i.e. expected formal oxidation state: trivalent $KCu(biuret)_2$, where biuret indicates $H_2NCONHCONH_2$, v=3, Cu $3d^8$ configuration; pure divalent insulating CuO v=2, Cu $3d^9$ configuration; and Cu_2O v=1, Cu $3d^{10}$ configuration. The spectra are shown in fig. 2. The energy scale has been normalized by fixing the maximum of the white line in CuO at 931.2 eV.[16]

The white line of CuO can be fitted by a simple Lorentzian with full width 0.95 eV. No high energy shoulder is observed in agreement with the single ground state localized configuration $3d^9$.

The spectrum of $KCu(biuret)_2$ shows a satellite at higher energy well separated from the white line. The results of the fitting of the white lines is shown in fig. 3. The white lines show a red shift with increasing oxidation state. From 931.2 eV in CuO, to 931.1 eV in the superconductor and to 930.8 eV in the trivalent compound $KCu(biuret)_2$. The width increases from 0.95 eV in CuO, to 1.25 eV in the superconductor, where it becomes asymmetric and 1.2 eV in $KCu(biuret)_2$. These white lines are clearly due to a similar electronic transition from Cu $2p^6$ $3d^9$ to Cu $2p^5$ $3d^{10}$ (i.e. $\underline{2p}3d^{10}$ final state) within the atomic potential of the

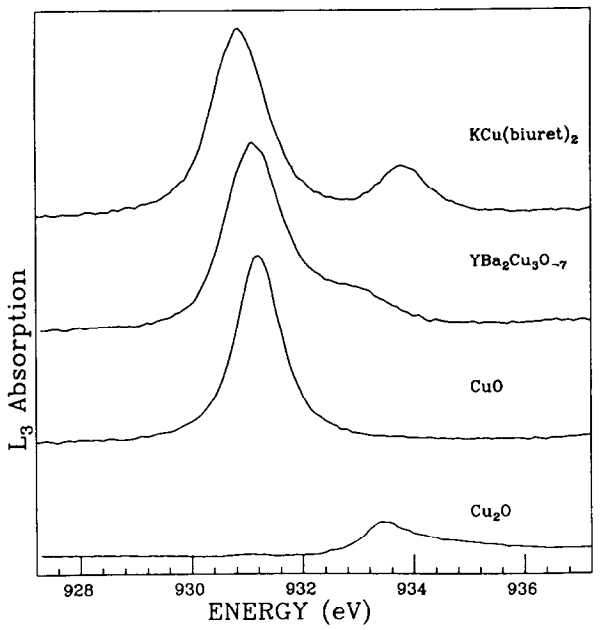

Fig.2 Cu L_3-edge of the samples, from top to bottom: trivalent Cu compound KCu (biuret)$_2$ (upper curve), high T_c superconducting $YBa_2Cu_3O_{6.9}$ sample with T_c=91K, pure divalent insulating CuO (curve c) and Cu_2O (curve d). The absorption coefficient is normalized to the absorption jump from below to above the white line energy.

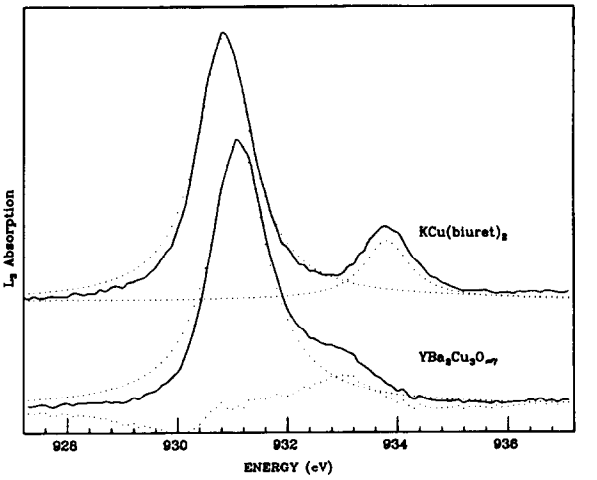

Fig.3 Results of the fitting of the white lines at the Cu L_3-edge spectra of high T_c superconducting $YBa_2Cu_3O_{6.5+x}$ ($x\sim 0.4$) and of KCu (biuret)$_2$. The energies of the maxima of the two Lorentzians for the spectrum of KCu (biuret)$_2$ are 930.8 eV and 933.7 eV with a full width of 1.2 eV and 1.05 eV respectively. The spectrum of $YBa_2Cu_3O_{6.9}$ is fitted with a Lorentzian at 931.1 eV and the residue obtained by subtracting the Lorentzian shows a maximum at ~933 eV.

Cu^{2+} ions. In fact for bivalent Cu compounds the white line has been observed to shift to lower energies by increasing the electronegativity of the ligand.[16]

The energy of the electronic transitions from Cu $2p^63d^8$ (for Cu^{3+} ions) to Cu $2p^53d^9$ (i.e. $\underline{2p}3d^9$) final state are expected to be shifted in comparison with the $\underline{2p}3d^{10}$ final state by the Coulomb interaction U_{cd} between 2p core hole and 3d electrons. The Cu 2p X-ray photoelectron spectrum of $YBa_2Cu_3O_{6.5+x}$($x\sim 0.4$)[22] shows a clear spectroscopical peak due to the $\underline{2p}3d^9$ final state configuration at ~942 eV. At this energy in the x-ray absorption spectrum of $YBa_2Cu_3O_{6.5+x}$ ($x\sim 0.4$) in fig. 1 there is no structure. Also in the trivalent model compounds there is no structure that can be associated with $\underline{2p}3d^9$ final state configuration.

The spectra of $YBa_2Cu_3O_{6.5+x}$ ($x\sim 0.4$) and of the KCu(biuret)$_2$ show a new feature at 933 eV and 933.7 eV respectively in comparison with bivalent Cu compounds. In fig. 3 it is clear that in $YBa_2Cu_3O_{6.5+x}$ ($x\sim 0.4$) there is an overlap between this broad feature at 933 eV and the white line, while in the insulating KCu(biuret)$_2$ compound they are completely separated by 3 eV.

This feature at 933 eV is characteristic of the metallic state of $YBa_2Cu_3O_{6.5+x}$($x\sim 0.4$) which exhibits superconductivity below 91K. In fact this 933 eV feature was observed to become undetectable in a sample prepared in air that shows a semiconducting behaviour and no superconductivity.

In order to show that the 933 eV peak is quenched with decreasing the oxygen content x we have reduced a sample by heating it in vacuum for 2 h at 400 °C. The 933 eV peak is reduced by the heat treatment as showed in fig. 4 where the spectra of the same sample before and after the heating in vacuum are compared. The difference spectrum between the heated and not heated sample shows a clear maximum at 933 eV and this feature overlaps the high energy side of the white line.

The difference spectrum in fig. 4 shows the lineshape of the derivative of the white line which can be assigned to a very small energy shift of the white line induced by sample reduction. This shift is in the expected direction but it is smaller than experimental resolution of 0.1 eV.

In order to assign the final state configuration of the 933 eV feature we have measured the spectrum of the Cu_2O

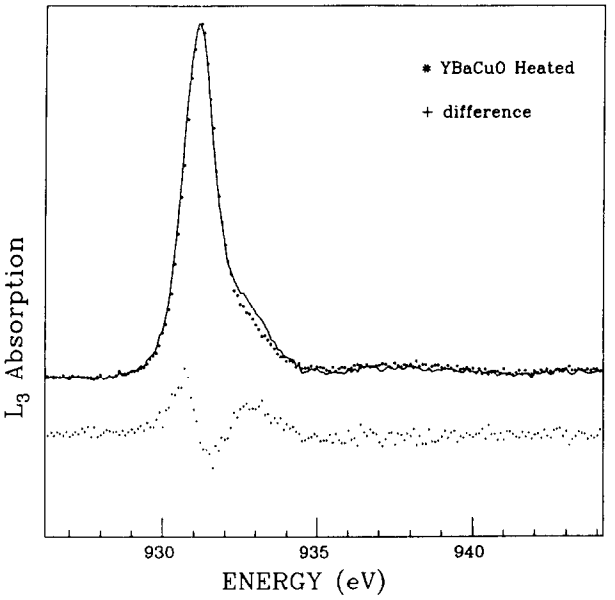

Fig.4 Cu L_3 edge x-ray absorption spectra of a second powder sample $YBa_2Cu_3O_{6.5+x}$ ($x\sim0.4$), solid line, and after decreasing the additional oxygen content x by heating the sample at 400 °C for two hours in vacuum, (dotted line). The lower curve shows the difference spectrum after having normalized the two white lines. The difference has been multiplied by a factor 2 and plotted in the same scale. There is clear evidence that the peak at 933 eV is quenched by decreasing x.

which shows a weak peak at threshold in fig.2. This peak is due to the an exciton for transition from the 2p core level to the first unoccupied 4s states of the conduction band i.e. $\underline{2p}3d^{10}4s^1$ final state configuration. This peak is at 933.4 eV in the Cu_2O spectrum.[19]

The Cu $2p_{3/2}$ XPS spectrum of high T_c superconductor $YBa_2Cu_3O_{6.5+x}$($x\sim0.4$) shows the main line at 933.2 eV.[22] This XPS line is due to the $2p3d^{10}\underline{L}$ final state determined by electronic charge transfer from the oxygen derived band to the Cu 3d orbitals leaving a hole in the oxygen band $\underline{L}$.

The energy of the peak at 933 eV in the L_3 spectrum of $YBa_2Cu_3O_{6.5+x}$($x\sim0.4$) is close to both $\underline{2p}3d^{10}\underline{L}$ and $\underline{2p}3d^{10}4s^1$ final state configuration.

For the $\underline{2p}3d^{10}\underline{L}$ final state the initial state is the $3d^9\underline{L}$. This configuration in the ground state is expected if there are not Cu^{3+} ions. In fact if the hole is not present in the localized Cu 3d orbitals it should be present in the oxygen derived band. Therefore the $3d^9\underline{L}$ configuration i.e. $Cu^{2+}O^-$ pairs should be induced by additional oxygen. This process is possible if there is a large metal oxygen covalency and the energy separation between the delocalized ligand band and the localized metal orbital is negligible. This seems to be the case for the high T_c superconducting perovskites because both the metal 3d and the oxygen 2p band are vfery close in energy.[23] The energy width of these $3d^9\underline{L}$ excitations is given by the convolution of the wide oxygen 2p derived band and the narrow 3d states therefore these excitations are itinerant. The presence of the $3d^9\underline{L}$ configuration close to the Fermi level should be associated with the conductivity in this high correlated system with localized Cu states.

The hypothesis of the presence of itinerant $3d^9\underline{L}$ states is in agreement with the experimental findings of lack of Cu derived delocalized states[15] and with evidence of hole conductivity. The hole conductivity is indicated by the positive Hall effect in high T_c superconducting materials reported by F. Steglich at the Symposium on Superconductivity at high Temperature of EPS meeting, april 8, in Pisa and with the positive sign of the Seebeck effect found at room temperature in oxygen deficient perovskites.[5]

The presence of the $3d^9\underline{L}$ in the ground state predicts the presence of a new peak at the threshold of the oxygen K-absorption in defective superconducting materials due to electronic transitions from the oxygen 1s to the ligand hole which has oxygen 2p character (i.e. O $\underline{1s}\,\underline{L}^{+1}\,3d^9$ or $O\underline{1s}3d^9$) below the first peak in integer valent Cu oxides. A similar transition has been observed in defective nickel oxide $Ni_{1-x}O$ where no Ni^{3+} ions are observed.[23,24]

The assignment of the 933 eV peak to the $\underline{2p}3d^{10}4s^1$ final state configuration implies the presence of the $3d^{10}$ configuration in the ground state i.e. of Cu^+ ions. This is possible if $YBa_2Cu_3O_{6.5+x}$ is an intermediate interatomic valence system[20] (like CeO_2, PrO_2 and NiO) which is described by mixing of localized configurations $3d^9$ and $3d^{10}\underline{L}$ with large electron-electron correlation energy and large covalency of the copper-oxygen bond. Therefore the final state which contributes to the 933 eV feature is actually $\underline{2p}3d^{10}\underline{L}\,4s^1$

Incresing the additional oxygen x (giving $3d^9\underline{L}$ configuration) induces a the contraction of the Cu-O distance and the distortions of the crystalline structure and contractuion of the Cu-O bond length which increase the covalency of the Cu-O bond in such a way that the weight of the $3d^{10}\underline{L}$ configuration increases. In the insulating trivalent Cu compound both $3d^9\underline{L}$ and $3d^{10}\underline{L}$ should be present but the two configurations are separated by an energy gap while in the metallic state both states cross the Fermi level.

CONCLUSIONS

This experiment does not give evidence of $2p3d^8$ final states in the $L_{2,3}$ absorption spectrum indicating Cu^{3+} ions in the high T_c superconductor. The high oxidation state determined by the additional oxygen x is shown to give O^- ions.

The metallic phase which exhibits superconductivity shows an absorption peak at 933 eV which has been associated with the presence of holes in the oxygen derived valence band giving $3d^9\underline{L}$ configuration (Cu^{2+}-O^- pairs which should be diamagnetic electron-hole pairs) and the $3d^{10}\underline{L}$ configuration forming a continuum close to the Fermi level. These electronic states disappear by reducing the sample and by going in the semiconducting phase. The presence of the interatomic intermediate valence state due to mixing of the $3d^9$ and $3d^{10}\underline{L}$ configurations has been discussed.

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